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(54) FLUIDS SUITABLE FOR USE AS HYDRAULIC FLUIDS, ELECTRICAL OILS, HEAT TRANSFER FLUIDS AND REFRIGERANT OILS

(71) We, CASTROL LIMITED, a British Company, of Burmah House, Pipers Way, Swindon, Wiltshire, SN3 1RE, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

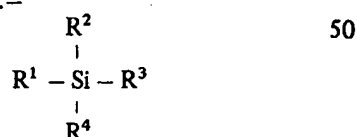
This invention relates to fluids suitable for use as hydraulic fluids, electrical oils, heat transfer fluids and refrigerant oils, hereinafter referred to as "functional fluids" and in particular to functional fluids based on hydrocarbon oils.

The performance of fluids based on hydrocarbon oils is often found in practice to be impaired by the presence of water, this problem being particularly acute when such fluids are used as hydraulic fluids e.g. in aviation or automobiles, or as electrical or refrigerant oils. In hydraulic fluids for example, water may be present as the result of condensation or inadequate drying of the hydraulic system prior to filling or subsequently, by entry through worn seals and it has been found that the effective vapour lock temperature (VLT) of the fluid can be reduced to the boiling point of water even by the presence of very minor amounts of water, e.g. of the order of 0.5%. This constitutes a serious deficiency with particularly dangerous consequences in those systems which are brake systems or central hydraulic systems including brake systems. Furthermore, in electrical oils the presence of free water increases conductivity and thus promotes electrical discharge and in refrigerant oils water may separate out as ice crystals.

We have now found that in certain silicon compounds are useful as water scavengers in functional fluids based on hydrocarbon oils and may thus alleviate the problems outlined above as previously encountered in the use of such fluids.

According to the present invention there is provided a functional fluid as hereinbefore defined comprising a major amount (by weight) of a hydrocarbon oil and a minor amount (by weight) of an oxysilane compound having the

general formula:—

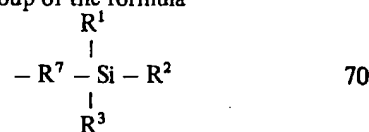


wherein:—

(i) R^1 is alkyl, preferably containing from 1 to 20, more preferably 1 to 4, carbon atoms; alkenyl, preferably containing from 2 to 20 carbon atoms; aryl, preferably phenyl; alkaryl or aralkyl, preferably containing from 7 to 20 carbon atoms; or alicyclic, preferably containing from 6 to 20 carbon atoms;

(ii) R^2 and R^3 are each independently a group as defined for R^1 or a group of the formula — (OR⁵)_n — OR⁶;

(iii) R^4 is a group of the formula — (OR⁵)_n — OR⁶ or a group of the formula



wherein R^1 , R^2 and R^3 are independently as defined above;

(iv) R^5 is alkylene, preferably containing from 1 to 15, more preferably 1 to 4, carbon atoms, especially ethylene, propylene or butylene; and each R^5 may be the same as or different from any other group R^5 ;

(v) R^6 is alkyl, preferably containing from 1 to 20, more preferably 4 to 18, especially 6 to 15, carbon atoms; alkenyl, preferably containing from 2 to 20 carbon atoms; aryl, preferably phenyl; alkaryl or aralkyl, preferably containing from 7 to 20 carbon atoms; or alicyclic, preferably containing from 6 to 20 carbon atoms; and each R^6 may be the same as or different from any other group R^6 ;

(vi) n is zero or an integer, preferably zero or an integer from 1 to 30, more preferably 1 to 10, particularly 1 to 4; and each n may be the same as or different from any other n ; and

(vii) R^7 is a direct linkage or a group of the formula — (OR⁵)_n — wherein R^5 and n are independently as defined above, provided that when R^7 is a direct linkage at least one

group of R^2 or R^3 is a group of the formula $-(OR^5)_n-OR^6$

The water scavenging action of the oxysilane compounds defined above has been found to be improved in the presence of an amine and functional fluids in accordance with the invention which additionally comprise as an optional constituent a small amount, e.g. from 0.5 to 20%, more particularly from 1 to 10%, by weight of an amine are accordingly preferred. Many amines have been found to be suitable, including primary, secondary and tertiary amines, especially those containing a total of at least 5 carbon atoms. Amines which have been found to be particularly useful include Primene 81 R and Primene JMT which are commercially available primary amines with two methyl groups on the alpha carbon atom. (Primene is a Registered Trade Mark).

Other amines which may be useful are Mannich bases formed by condensation of an amine and formaldehyde with a phenol previously alkylated with di- or polyisobutylene; polyisobutenylsuccinimides derived from di- or polyamines; or amides derived from di- or polyalkylene polyamines and polyisobutenyl substituted monocarboxylic acids.

The amount of oxysilane compound employed in the functional fluids of the invention may vary over a wide range, e.g. from 0.1% to 50% by weight based on the total weight of the fluid.

More particularly, the amount will depend on several factors such as:-

- (a) the nature of the fluid base-stock;
- (b) the normal use of the functional fluid;
- (c) the physical properties required of the finished functional fluid; and
- (d) the amount of water likely to be encountered by the fluid in its final use.

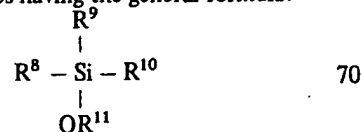
In hydraulic fluids for instance the oxysilane compound would normally be employed in an amount of from 1 to 35%, preferably from 10 to 20%, by weight. On the other hand, in refrigerant oils, electrical oils and heat transfer fluids the preferred amount of oxysilane compound would generally be somewhat lower e.g. from 0.1 to 5.0% by weight.

The oxysilane compounds employed in the fluids of the present invention may be readily prepared from chlorosilanes by reaction with appropriate hydroxy compounds using well known techniques. A detailed description of such preparative methods is to be found in J. Amer. Chem. Soc. 80, 1733 (Wright et al) and 68, 70 (Peppard et al).

The hydrocarbon oil used as base-stock in the functional fluids of the invention is preferably a mineral oil, whether derived from crude oil or synthesised from hydrocarbons. Specific examples of such oils are hydrorefined mineral oils and alkylated benzenes.

The functional fluids of the invention may optionally comprise, e.g. in an amount from 0.1 to 30%, preferably 0.5 to 20%, by weight based

on the total weight of the fluid, one or more silane derivatives having the general formula:-

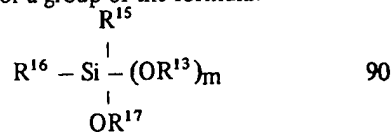


wherein:

(a) R^8 is a group of the formula $R^{12} - (OR^{13})_m - OR^{14}$; 75

(b) each of R^9 and R^{10} is independently alkyl, preferably containing from 1 to 18 carbon atoms, more preferably methyl; alkenyl, preferably containing from 2 to 18 carbon atoms; aryl, preferably phenyl; alkaryl, preferably alkyl substituted phenyl in which the alkyl substituent contains from 1 to 12 carbon atoms; or aralkyl, preferably benzyl; a group of the formula $-OR^{11}$; or a group of the formula $R^{12} - (OR^{13})_m - OR^{14}$; 80

(c) R^{11} is a group of the formula $R^{12} - (OR^{13})_m$ - or a group of the formula:- 85



and each R^{11} may be the same as or different from any other group R^{11} ;

(d) R^{12} is alkyl, preferably containing from 1 to 18 carbon atoms; alkenyl, preferably containing from 2 to 18 carbon atoms; aryl, preferably phenyl; alkaryl, preferably alkyl substituted phenyl in which the alkyl substituent contains from 1 to 12 carbon atoms; or aralkyl, preferably benzyl; and each R^{12} may be the same as or different from any other group R^{12} ; 100

(e) R^{13} is an alkylene group, preferably containing from 1 to 15, more preferably 1 to 4, carbon atoms, especially ethylene or propylene; and each R^{13} may be the same as or different from any other group R^{13} ; 105

(f) R^{14} is an alkylene group, preferably containing from 1 to 15, more preferably 1 to 6, carbon atoms; and each R^{14} may be the same as or different from any other group R^{14} ; 110

(g) m is zero or an integer, preferably zero or an integer of from 1 to 4; and each m may be the same as or different from any other m ;

(h) each of R^{15} and R^{16} is independently alkyl, preferably containing from 1 to 18 carbon atoms, more preferably methyl; alkenyl, preferably containing from 2 to 18 carbon atoms; aryl, preferably phenyl; alkaryl, preferably alkyl substituted phenyl in which the alkyl substituent contains from 1 to 12 carbon atoms; or aralkyl, preferably benzyl; a group of the formula $-OR^{17}$; or a group of the formula $R^{12} - (OR^{13})_m - OR^{14}$; and 115

(i) R^{17} is a group of the formula $R^{12} - (OR^{13})_m$ - and each R^{17} may be the same as or different from any other group R^{17} . 125

The above defined silane derivatives of Formula II are more fully described in our U.K. Patent Application No. 48009/75 (Serial No. 130

1577715) (equivalent to German Offenlegungsschrift 26 52 719) to which reference may be made for further details.

It will be understood that the functional fluids of the present invention may contain small amounts e.g. 0.05% to 20%, particularly 0.1 to 2%, by weight of additives conventionally employed in such fluids.

In a further aspect of the present invention there is provided a hydraulic system for transmitting power by hydraulic means which system contains as the hydraulic fluid, a functional fluid as hereinbefore described.

In yet another aspect of the present invention there is provided a method of operating a hydraulic system which comprises introducing into the hydraulic system as the hydraulic fluid a functional fluid as hereinbefore described and transmitting power by applying pressure to the hydraulic fluid.

The invention will now be illustrated by the following Examples:—

Examples 1 to 21

Functional fluids in accordance with the invention were formulated and subjected to the following tests:—

(a) Kinematic viscosities at -40°C , in centistokes (cS), were measured in the manner set forth in the current SAE J1703 specification;

(b) Rubber swell properties with respect to nitrile (HN 57) and urethane (HU723) rubbers were determined in the manner set forth in the BS 903 specification by measuring the increase in volume of 2.54 cm. square, 2 mm. thick rubber specimens after immersion in the test fluid at 70°C for 3 days.

(c) Vapour lock temperatures were determined by the Gilpin Vapour Lock Test as specified in SAE Paper 710 253 entitled "Operating Performance of Motor Vehicle Braking Systems as affected by Fluid Water Content", the Gilpin vapour lock temperature (VLT) being taken to correspond with the appearance of 3 ml of vapour. This test was performed upon fluids which had previously been subjected to a Humidity Test at a relative humidity (RH) of 80% and a temperature of about 23°C substantially as described in the FMVSS DOT 3/4 specification but extended to a 5 day period and without a reference fluid.

Details of the oxysilane compounds and proportions thereof in the fluids and of the results obtained in the above tests are given in Table 1.

In each case the fluid also contained 2% Primene JMT, a commercially available tertiary alkyl primary amine containing approximately 18 carbon atoms.

The hydrocarbon oil constituting the balance of the fluid was in each case a naphthenic mineral oil having the following characteristics:

Viscosity:— 130 cS at -40°F ; 3.5 cS at 100°F ; and 1.31 cS at 210°F .
 Pour Point:— $< -70^{\circ}\text{F}$.
 Boiling Point:— 248°C .
 Flash Point (closed):— 208°C .
 Aniline Point:— 76°C .

TABLE 1

Example No.	Silane	% by wt in blend	Viscosity @ -40°C (cS)	Rubber Swell Tests		Gilpin VLT ($^{\circ}\text{C}$)
				HN 57	HU 723	
1	$(\text{RO})_3\text{-Si-Me}$ R = 2-octyl	40	156.6	-4.0	-14	257
2	R = tridecyl	20	236.8	-1.1	2.0	233
3	R = $\text{Me}(\text{OCHCH}_2)\text{-}$ CH_3	10	139	0.46	3.9	241
4	$(\text{RO})_2\text{-Si}(\text{Me})_2$ R = n-octyl	8	97	6.6	4.0	227
5	R = tridecyl	4	590	-4.6	0.66	266
6	R = phenyl	20	115	17.9	20.3	197
7	R = $\text{CH}_3(\text{OCHCH}_2)_2\text{-}$ CH_3	50	94.9	7.6	8.1	234
8	$\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{O-Si}(\text{Me})_2$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_2\text{O}$ C_2H_5	45	68.6	2.5	5.1	234
9	CH_3 $\text{CH}_3(\text{OCHCH}_2)_2\text{O-Si}(\text{Me})_2$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_2\text{O}$ C_2H_5	35	96	5.2	—	245

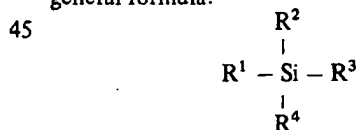
Table 1 (continued)

Example No.	Silane	% by wt in blend	Viscosity @ -40 (cS)	Rubber Swell Tests HN 57 HU 723	Gilpin VLT (°C)
5	C ₂ H ₅				70
10	(RO) - Si - (Me) ₃ R = 2 ethylhexyl	40	282	3.6 6.2	173
11	R = tridecyl	30	89.7	2.0 4.4	206
12	R = Me(OCH ₂ CH)- CH ₃	20	62.1	6.1 8.6	160
13	R = phenyl	10	75.1	5.7 12.2	179
15	CH ₃ (CH ₃) ₃ Si-(OCH ₂ CH) ₂₆ -OSi(CH ₃) ₃ * (phenyl) ₂ Si[O(CH ₂ CH ₂ O) ₃ CH ₃] ₂ CH ₃	30 15	743 300	-3.5 +0.65 2.9 3.8	167 223
16	methyl-Si-[O CH ₂ CH-CH ₂ CH ₂ CH ₂ CH ₃] ₂ phenyl C ₂ H ₅	30	208.1	1.7 3.2	247
25	R' Si(OR) ₃ R' = phenyl				90
17	R = 2-ethyl hexyl	25	212.3	0.2 2.4	249
18	R' = ethyl				
19	R = 2-methylcyclohexyl	25	331.7	-1.4 1.9	250
20	R' = ethyl				
21	R = benzyl	40	124.4	28.8 24.0	227
22	R' = Vinyl				
23	R = butyl triglycol	35	309.0	8.7 9.6	183
24	R' = 2,4,4-trimethylpentyl				
25	R = C ₄ H ₉ OCH ₂ CH ₂ -	30	140.7	1.2 4.2	235

* The formula given is an ideal one. The product was in fact derived from a mixture of polypropylene glycols of average molecular weight of about 1500.

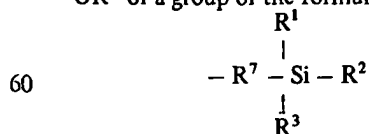
WHAT WE CLAIM IS:-

1. A functional fluid as hereinbefore defined comprising a major amount by weight of a hydrocarbon oil and a minor amount by weight of an oxysilane compound having the general formula:-



wherein:

- (i) R¹ is alkyl, alkenyl, aryl, alkaryl, aralkyl or alicyclic;
(ii) R² and R³ are each independent a group as defined for R¹ or a group of the formula -(OR⁵)_n-OR⁶;
(iii) R⁴ is a group of the formula -(OR⁵)_n-OR⁶ or a group of the formula:-



wherein R¹, R² and R³ are independently as defined above,

- (iv) R⁵ is alkylene; and each R⁵ may be the

same as or different from any other group R⁵;
(v) R⁶ is alkyl, alkenyl, aryl, alkaryl, aralkyl or alicyclic; and each R⁶ may be the same as or different from any other group R⁶;

(vi) n is zero or an integer; and each n may be the same as or different from any other n; and

(vii) R⁷ is a direct linkage or a group of the formula -(OR⁵)_n-O- wherein R⁵ and n are independently as defined above, provided that when R⁷ is a direct linkage at least one group R² or R³ is a group of the formula -(OR⁵)_n-OR⁶.

2. A fluid as claimed in claim 1 wherein R¹ is alkyl containing from 1 to 20 carbon atoms, alkenyl containing from 2 to 20 carbon atoms, phenyl, alkaryl or aralkyl containing from 7 to 20 carbon atoms or alicyclic containing from 6 to 20 carbon atoms.

3. A fluid as claimed in claim 1 wherein R¹ is alkyl containing from 1 to 4 carbon atoms.

4. A fluid as claimed in any one of the preceding claims wherein R⁵ is alkylene containing from 1 to 15 carbon atoms.

5. A fluid as claimed in claim 4 wherein R⁵ is alkylene containing from 1 to 4 carbon atoms.

6. A fluid as claimed in claim 5 wherein R⁵

is ethylene, propylene or butylene.

7. A fluid as claimed in any one of the preceding claims wherein R^6 is alkyl containing from 1 to 20 carbon atoms, alkenyl containing from 2 to 20 carbon atoms, phenyl, alkaryl or aralkyl containing from 7 to 20 carbon atoms or alicyclic containing from 6 to 20 carbon atoms.

8. A fluid as claimed in claim 7 wherein R^6 is alkyl containing from 4 to 18 carbon atoms.

9. A fluid as claimed in claim 8 wherein R^6 is alkyl containing from 6 to 15 carbon atoms.

10. A fluid as claimed in any one of the preceding claims wherein n is zero or an integer of from 1 to 30.

11. A fluid as claimed in claim 10 wherein n is zero or an integer of from 1 to 10.

12. A fluid as claimed in claim 11 wherein n is zero or an integer of from 1 to 4.

13. A fluid as claimed in claim 1 wherein the oxysilane is selected from:-

(i) compounds of the formula $(RO)^3 - Si - CH_3$ wherein R is 2-octyl, tridecyl or $CH_3(OCHCH_2)_2$;

(ii) compounds of the formula $(RO)_2 - Si - (CH_3)_2$ wherein R is n -octyl, tridecyl, phenyl or $CH_3(OCHCH_2)_2$;

(iii) the compound having the formula $C_4H_9OCH_2CH_2O - Si(CH_3)_2$;

(iv) the compound having the formula

$CH_3(OCHCH_2)_2O - Si(CH_3)_2$

(v) compounds of the formula $(RO) - Si - (CH_3)_3$ wherein R is 2-ethylhexyl, tridecyl, phenyl or $CH_3(OCHCH_2)_2$;

(vi) the compound having the formula

$(CH_3)_3Si - (OCH_2CH)_6 - OSi(CH_3)_3$;

(vii) the compound having the formula $(phenyl)_2Si[O(CHCH_2O)_3CH_3]_2$;

(viii) the compound having the formula $CH_3 - Si[OCH_2CH - CH_2CH_2CH_2CH_3]_2$; and

(ix) compounds of the formula $R' - Si(OR)_3$, wherein R' is phenyl and R is 2-ethylhexyl, R' is ethyl and R is 2-methylcyclohexyl, R' is ethyl

and R is benzyl, R' is vinyl and R is butyl tri-glycol or R' is 2,4,4-trimethylpentyl and R is $C_4H_9OCH_2CH_2$;

14. A fluid as claimed in any one of the preceding claims which additionally comprises an amine in an amount of from 0.5 to 20% by weight.

15. A fluid as claimed in claim 14 wherein the amine is present in an amount of from 1 to 10% by weight.

16. A fluid as claimed in claim 14 or claim 15 wherein the amine is a primary, secondary or tertiary amine containing at least 5 carbon atoms.

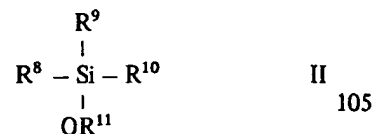
17. A fluid as claimed in any one of claims 14 to 16 wherein the amine is selected from Mannich bases formed by condensation of an amine and formaldehyde with a phenol previously alkylated with di- or polyisobutylene; polyisobutenylsuccinimides derived from di- or polyamines; and amides derived from di- or polyalkylene polyamines and polyisobutenyl substituted monocarboxylic acids.

18. A fluid as claimed in claim 16 wherein the amine is a primary amine having two methyl groups on the alpha carbon atom.

19. A fluid as claimed in any one of the preceding claims wherein the hydrocarbon oil is a mineral oil.

20. A fluid as claimed in any one of claims 1 to 18 wherein the hydrocarbon oil is hydro-refined mineral oil or an alkylated benzene.

21. A fluid as claimed in any one of the preceding claims which additionally comprises one or more silane derivatives having the general formula:-

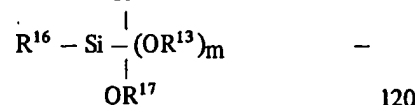


wherein:

(a) R^8 is a group of the formula $R^{12} - (OR^{13})_m - OR^{14}$;

(b) each of R^9 and R^{10} is independently alkyl, alkenyl, aryl, alkaryl, aralkyl, a group of the formula $-OR^{11}$ or a group of the formula $R^{12} - (OR^{13})_m - OR^{14}$;

(c) R^{11} is a group of the formula $R^{12} - (OR^{13})_m$ - or a group of the formula:-



and each R^{11} may be the same as or different from any other group R^{11} ;

(d) R^{12} is alkyl, alkenyl, aryl, alkaryl or aralkyl; and each R^{12} may be the same as or different from any other group R^{12} ;

(e) R^{13} is an alkylene group; and each R^{13} may be the same as or different from any other group R^{13} ;

(f) R^{14} is an alkylene group; and each R^{14} may be the same as or different from any other

- group R^{14} ;
- (g) m is zero or an integer, and each m may be the same as or different from any other m ;
- (h) each of R^{15} and R^{16} is independently alkyl, alkenyl, aryl, alkaryl, aralkyl, a group of the formula $-OR^{17}$ or a group of the formula $R^{12} - (OR^{13})_m - OR^{14}$; and
- (i) R^{17} is a group of the formula $R^{12} - (OR^{13})_m$ - and each R^{17} may be the same as or different from any other group R^{17} .
22. A fluid as claimed in claim 21 wherein each of R^9 and R^{10} is independently alkyl containing from 1 to 18 carbon atoms, alkenyl containing from 2 to 18 carbon atoms, phenyl, alkyl substituted phenyl in which the alkyl substituent contains from 1 to 12 carbon atoms, benzyl, a group of the formula $-OR^{11}$ or a group of the formula $R^{12} - (OR^{13})_m - OR^{14}$; R^{12} is alkyl containing from 1 to 18 carbon atoms, alkenyl containing from 2 to 18 carbon atoms, phenyl, alkyl substituted phenyl in which the alkyl substituent contains from 1 to 12 carbon atoms or benzyl; R^{13} is an alkylene group containing from 1 to 15 carbon atoms; R^{14} is an alkylene group containing from 1 to 15 carbon atoms; m is zero or an integer of from 1 to 4; and each of R^{15} and R^{16} is independently alkyl containing from 1 to 18 carbon atoms, alkenyl containing from 2 to 18 carbon atoms, phenyl, alkyl substituted phenyl in which the alkyl substituent contains from 1 to 12 carbon atoms, benzyl, a group of the formula $-OR^{17}$ or a group of the formula $R^{12} - (OR^{13})_m - OR^{14}$.
23. A fluid as claimed in claim 21 or claim 22 wherein the silane derivative of formula II is present in an amount of from 0.1 to 30% by weight, based on the total weight of the fluid.
24. A fluid as claimed in claim 23 wherein the silane derivative of formula II is present in an amount of from 0.5 to 20% by weight.
25. A fluid as claimed in any one of the preceding claims wherein oxysilane compound of formula I is present in an amount of from 0.1 to 50% by weight based on the total weight of the fluid.
26. A fluid as claimed in claim 25 wherein oxysilane compound of formula I is present in an amount of from 1 to 35% by weight.
27. A fluid as claimed in claim 26 wherein oxysilane compound of formula I is present in an amount of from 10 to 20% by weight.
28. A fluid as claimed in claim 25 wherein oxysilane compound of formula I is present in an amount of from 0.1 to 5.0% by weight.
29. A fluid as claimed in any one of the preceding claims which additionally comprises one or more additives conventionally employed in hydraulic fluids, refrigerant oils, electrical oils or heat transfer fluids.
30. A fluid as claimed in claim 1, substantially as hereinbefore described in any one of Examples 1 to 21.
31. A hydraulic system for transmitting power by hydraulic means which system contains as the hydraulic fluid, a functional fluid as claimed in any one of the preceding claims.
32. A method of operating a hydraulic system which comprises introducing into the hydraulic system as the hydraulic fluid, a functional fluid as claimed in any one of claims 1 to 30 and transmitting power by applying pressure to the hydraulic fluid.
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